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Energy Procedia 142 (2017) 136–141

Energy Procedia

www.elsevier.com/locate/procedia

9th International Conference on Applied Energy, ICAE2017, 21-24 August 2017, Cardiff, UK

Study on the ignition behavior and kinetics of combustion of biomass

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Abstract

Understanding the combustion behavior of biomass is essential to plant design and production control. In this work, we used thermogravimetric analysis (TGA) to study milled straw samples of different particle sizes in atmospheres of nitrogen and air. The ignition temperature was found to be 350℃, and the results were found to be insensitive to the particle size, which ranged from 63 μm to 2000 μm. In addition, a furnace balance system was used to study the impacts of particle size on the combustion of biomass and compare with TGA results. The activation energies of combustion were determined to be 54.37 kJ mol^{-1} for straw pellets and 49.94 kJ mol^{-1} for the milled straw. Further calibration of the furnace-balance system will be carried out in future to obtain more precise and reliable results for biomass fuel characterization.

Peer-review under responsibility of the scientific committee of the 9th International Conference on Applied Energy.

Keywords: Biomass; ignition; kinetic; particle size

1. Introduction

Biomass is considered to be a renewable, carbon-neutral fuel; it holds the promise of acting as an alternative energy resource that can address the worldwide energy crisis. One efficient method to convert biomass to energy is by direct combustion [1]; however, several issues face current biomass combustion furnaces, such as low thermal efficiency, heat load instability and slagging [2]. Ignition is the crucial step that initiates combustion, and it influences boiler operation, energy efficiency, and emissions. Thus, the study of ignition behaviour of biomass is important to optimizing biomass combustion. Hence, a deep knowledge of the thermal behaviour of biomass is critical to assess

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1876-6102
Peer-review under responsibility of the scientific committee of the 9th International Conference on Applied Energy.
10.1016/j.egypro.2017.12.022

the feasibility, design, and scaling of industrial biomass conversion applications [3, 4].

Thermogravimetric analysis (TGA) is commonly used to study the thermal behaviour of solid fuels. Several studies have been carried out with TGA to reveal the ignition behaviour of coal, biomass and coal-biomass blending [5-7]. Grotkjær et al. [8] reported that the ignition temperature of the solid fuel is highly dependent on the particle size, while the sample studied in TGA is normally at fine sizes and the testable quantity is small, which is difficult to study the impact of particle size on ignition behaviour, this has also been reported by Li et al. [9] To distinguish the influence of particle size and shape on thermal behaviour of biomass, a high-temperature furnace-balance system (FBS) is developed and tested.

The aim of this work is to investigate the influence of particle size on the ignition behaviour of straw using TGA and determine the combustion kinetic parameters of different sizes of biomass using a high-temperature furnace-balance system.

2. Materials and methods

2.1 Materials

Straw pellets were milled and screened into three sizes: 1000-2000 μm, 315-500 μm and 63-80 μm. The results from proximate and ultimate analysis of the samples are summarized in Table 1.

Table 1. Proximate and ultimate analysis of sample.

wt, %	Sample tested in TGA		Sample tested in furnace	
M_{ad} (moisture content)	5.6		9.3	
V_d (volatile matter)	57.92		67.8	
A_d (ash content)	7.92		6.7	
FC_d (fixed carbon)	37.16		16.2	
C (*db*)	55.92		45.2	
H (*db*)	5.02		5.25	
O (*db*)	30.48		41.2	
N (*db*)	0.44		0.71	

*db=dry basis

2.2 Estimations of the ignition temperature using TGA

The Netzsch STA 449 F3 Jupiter, which is a high speed furnace, was used to obtain the thermogravimetric (TG) and differential thermogravimetric (DTG) curves for the milled straw samples. The ignition temperature is identified as the lowest temperature at which a solid fuel starts to ignite in air without the aid of an external ignition source. In theory, it is the temperature to which a fuel-air mixture must be increased so that the heat evolved by the exothermic reactions of the system will just overbalance the rate at which heat is discharged to the surroundings [10]. By comparing the behaviour of fuels in an oxidative and an inert atmosphere, the mechanism of ignition can be examined, and through the study of TG and DTG curves, the ignition temperature can be determined. A common approach is to identify the ignition temperature as the temperature at which the weight loss curves in the combustion (in an oxidative atmosphere) and pyrolysis (in an inert atmosphere) experiments diverge [11, 12].

2.3 The high temperature furnace-balance system

The high-temperature furnace balance system (FBS) is a combined device, the furnace is ThermConcept High-Temperature furnace comes with Eurotherm 3208 controller, it can test the combustion of different samples in different sizes and shapes under different conditions and obtain the solid products; the connected balance is Sartorius laboratory balance, which can record the weight change of sample during the tests. The balance is connected to a platform with a thermal insulation tube. Figure 1 shows a picture of the device and a sketch of the connection. During the test, temperature of the furnace is governed by a heating program and data are collected in real-time.

5 g straw pellets (each pellet is about 0.7-1 g in mass, 4 cm in length and 0.5 cm in diameter) and 5 g milled straw pellets were tested in the furnace-balance system to study the heating characteristics of equipment and to calculate the combustion kinetics parameters: activation energy, *E* and pre-exponential factor *A*. The samples were

air-dried at ambient till the weight is constant. For each test, the crucible with a sample is placed on the platform inside the furnace, and the weight change of sample during combustion will be continuously recorded. In this way, thermogravimetric data can be collected.

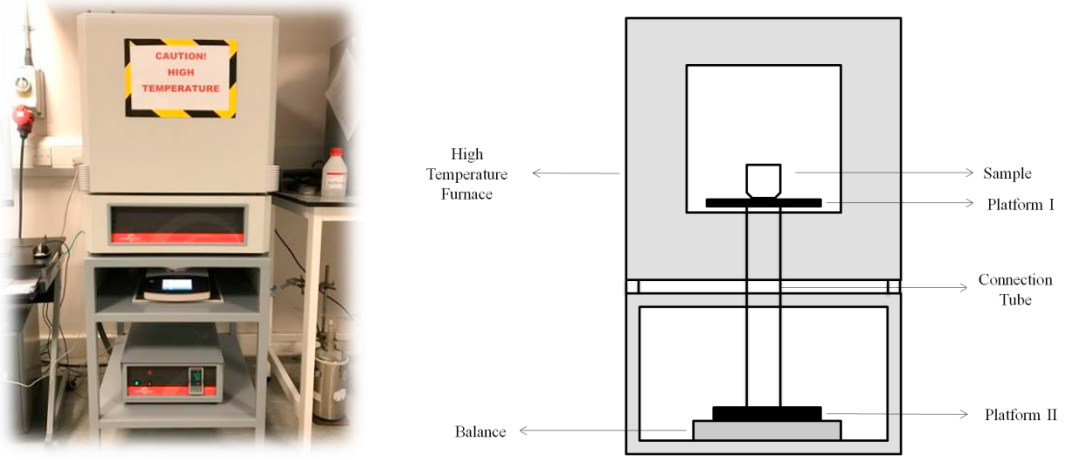

Fig.1. Furnace-balance system (left) and schematic diagram (right).

2.4 Modelling reaction kinetics

The kinetics of biomass combustion can be expressed by the following canonical equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Aexp\left(\frac{-E}{RT}\right)f(\alpha) \quad (1)$$

where T is the absolute temperature, R is the universal gas constant, $f(\alpha)$ is the conversion function, and α is the conversion rate, which represent the relationship between initial mass m_0, final mass m_∞, and current mass m of the system, as given below:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (2)$$

When the heating rate $\beta = dT/dt$ is constant, Eq. (1) can be integrated to yield:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T dT exp\left(-\frac{E}{RT}\right) \quad (3)$$

where $g(\alpha)$ is an integration function., consequently, Eq. (3) can be approximated by :

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (4)$$

The term $f(\alpha)$ depends on the conditions and the stage of the reaction under study. The kinetics of combustion was largely described by first order Arrhenius law [13]. Combustion is a complicated process. It is normally divided into three different reaction stages [14], two parallel reactions with three reaction stages [15], or, more recently, a two stage reaction with a first step that occurs at lower temperature and is followed by the combustion of char at higher temperature [16]. In the mass loss curves shown in Figure 3, there are two steep decreases in the curves obtained from the furnace-balance system measurements. This implies that the combustion process can be divided into two steps (low and high temperature), each governed by first order Arrhenius law [17]. In this case $f(\alpha) = (1-\alpha)$ and, as a result, $g(\alpha) = -\ln(1-\alpha)$, and for most system $RT/E \ll 1$.

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] \approx \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (5)$$

In the Coats-Redfern method[18] for obtaining the kinetic parameters of a reaction, the left side of Eq. (5) is plotted against T^{-1} for the data from a single heating curve, which leads to a line; E can be obtained from the slope

of this line, and *A* derived from its intercept.

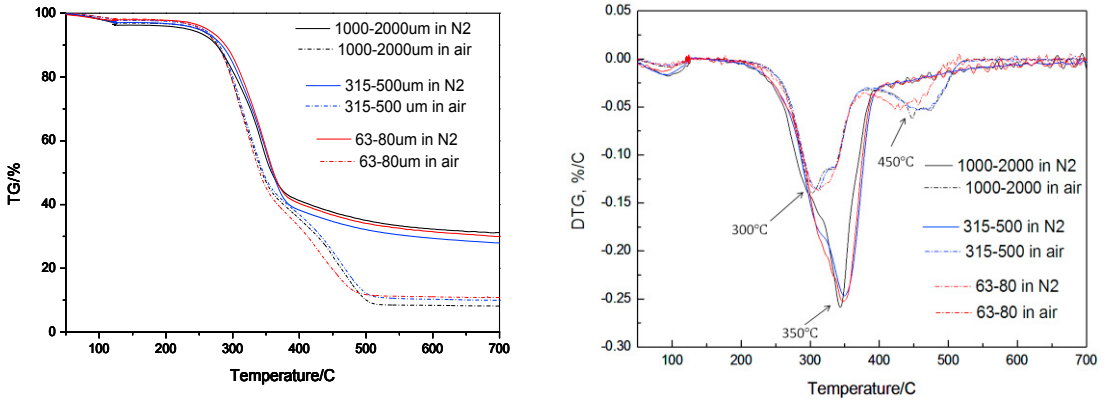

Fig.2. Thermal characteristics of straw under air and N_2 in TGA: TG curves (left) and DTG curves (right).

3. Results and discussion

3.1 Thermal characteristics of straw in air and N_2 environments using TGA

The thermal characteristics of different sizes of straw under air and N_2 conditions are examined using TGA, the heating rate is 1200℃ h^{-1}. The results are presented in Fig. 2. The weight loss curves between the samples in the air and N_2 environments show little differences within the temperature range from ambient to about 350℃. This implies that, in the first stage release of volatile matter, temperature is the dominant factor, rather than the presence of oxygen. The difference of thermal conductivity of air and N_2 may be the reason for the slight deviations [9]. For the samples under air, a second sharp drop in weight occurs at temperatures higher than 350℃, due to the combustion of char which occurs after the release of volatile matters. The weight loss of samples under N_2 is slower at these temperatures. The difference between these two conditions is similar to the difference between the ash content and fixed carbon in straw. According to the previous statement, 350℃ is the diverging point, which means that the ignition point of the straw is 350℃.

The influence of particle size could not really be observed for the samples in either the air or N_2 environments. The curves are nearly overlapped for temperatures below 350℃. This is the stage of volatile matters release and dominated by temperature. For temperatures higher than 350℃, the slight differences among the curves under each condition may be caused by the different content of mineral matters and distribution of fixed carbon. This might also be indicated in DTG curves, the particle size has caused little difference among neither the only peak under the N_2 condition nor the two peaks under the air condition. In an N_2 environment, the maximum weight loss temperature is 350℃, and in an environment, it is 300℃ and 450℃ in the first and second stage, respectively.

3.2 Thermal characteristics of straw in an air atmosphere using the furnace-balance system

The milled straw samples and single large pellets were tested in using TGA and furnace-balance system under the same combustion conditions. The heating rate was 1000℃ h^{-1}; mass loss curves and derivative mass loss curves are shown in Fig. 3. There is a clear difference between the mass loss curves obtained from TGA and FBS. In the drying stage, there is no obvious drop in the TGA measurements. Only 10 mg of sample was tested in this device; the sample was first milled and air dried, and, consequently, there is not much moisture content left. On the other hand, the sample tested in the FBS was about 5 g; the moisture loss during the pre-treatment process was relatively small, and according to the results, the mass loss in the drying stage was about 8% for both the fine particle sample and the large pellet sample, which is within the range of the proximate analysis. As the temperature increases to the volatile matter release stage, there is a delay of mass loss observed in the FBS. The delay may be due to the large volume of the furnace chamber, which is 10 L; it takes more time to heat and reach the target temperature than in the TGA. Also, the sample in the furnace is much larger; therefore, the heat transfer is not as efficient as that in the

TGA. The release of volatile matter from the sample occurs gradually from its surface to the inside of the sample container, but the total released volatile matter occupies almost the same volume as that in the TGA, which means the data acquired in this stage are reliable. However,

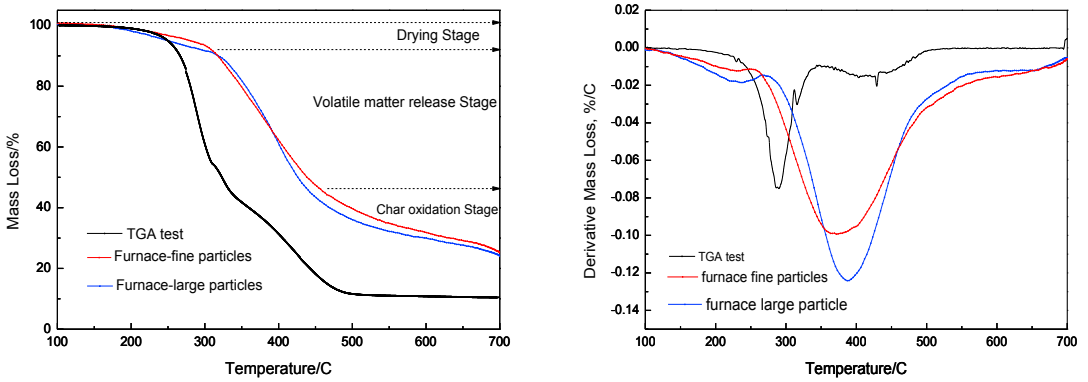

Fig. 3. Mass loss and derivative mass loss curves obtained from TGA and furnace-balance system.

in the char oxidation stage, the FBS takes a much longer time to burn out the remaining char ,which in turn reflects a much wider temperature range. The residues left in the FBS are about 15%, a little higher than that in the TGA, which is 10%. This may be caused by the different ash concentration and distribution in raw materials.

There is a difference in the mass loss curves between the fine particles and the large particles in the FBS tests, and it is also noticeable in the differential mass loss curves in Fig. 3. Particle size has big influence on the weight loss rate of biomass during combustion, which means the influence of particle size can be distinguished by the FBS. Further tests will be carried out to study the effect of different sizes and shapes of biomass on thermal behaviour.

3.3 Reaction kinetics

The mass loss data, most commonly measured using TGA, can be used to calculate the reaction kinetics parameters, which are important to understanding the thermal conversion process. A comparison of the kinetic parameters obtained between TGA and FBS can help to check the reliability of the data acquired from FBS, and also can help to calibrate the system. The kinetic results obtained from the calculation are shown in Table 2.

Table 2. Kinetic parameters obtained by Coats-Redfren method.

Sample		temperature range/ ℃	E, kJ mol^{-1}	A, s^{-1}	R^2
5g large particles	step 1	305-420	54.37	4.31E+06	0.9967
	step 2	480-650	5.57	1.55E+09	0.9464
5g fine particles	step 1	295-445	49.94	8.98E+06	0.9838
	step 2	465-655	9.03	1.66E+9	0.9828

The activation energy is the minimum energy required to start a reaction. The higher the value of E, the slower the reaction [19]. As discussed in Sec. 2.4, the process of combustion in FBS was divided into two steps, so in Step 1, activation energy for large particles is 54.37 kJ mol^{-1} and for fine particles is 49.94 kJ mol^{-1}, this means for the same material, the finer the sample, the lower the energy is needed to start to react. Besides, all calculated E are within the range reported by Alvarez [2], and the correlation coefficient of the tests are very high, so it shows that the first order kinetic model is feasible for the furnace-balance system too and the obtained kinetic parameters are reliable, and the milled fine particles requires lower energy to react than that of large particles.

For Step 2, E = 5.57 kJ mol^{-1} for large particle and 9.03 kJ mol^{-1} for fine particle, and the results are all smaller than that in Step 1, it means the char oxidation stage requires less energy to react than that in volatile matter release stage. Although the correlation coefficients obtained are very high for both samples in this stage, the activation

energy is much smaller than that obtained in Alvarez's study [2], but still within the approximate range from 1 to 180 kJ mol^{-1} [20].

3 Conclusion

In this paper, we investigated the ignition behaviour of biomass using TGA and a furnace-balance system. The ignition temperature was determined by identifying the point of divergence between the TG curves with and without the presence of oxygen. The TGA results were unable to identify the impact of particle size on the ignition behaviour of biomass.

By comparing the results obtained from TGA and furnace-balance system, it is possible to study the impact of particle size and shape on the biomass combustion process. The results of kinetic calculation agree well with each other, but the char oxidation stage is not well observed, and further enhancement of the FBS is needed. Future efforts should focus on the improvement of the accuracy of monitoring weight changes and atmosphere changes inside the furnace chamber.

Acknowledgements

The authors would like to thank the EU-Biofuels Research Infrastructure for Sharing Knowledge (BRISK) for their financial support of this work.

References

[1]. Nussbaumer, T., *Combustion and co-combustion of biomass: fundamentals, technologies, and primary measures for emission reduction.* Energy & fuels, 2003. **17**(6): p. 1510-1521.
[2]. Álvarez, A., et al., *Determination of kinetic parameters for biomass combustion.* Bioresource technology, 2016. **216**: p. 36-43.
[3]. Raveendran, K., A. Ganesh, and K.C. Khilar, *Pyrolysis characteristics of biomass and biomass components.* Fuel, 1996. **75**(8): p. 987-998.
[4]. Şensöz, S. and M. Can, *Pyrolysis of pine (Pinus brutia Ten.) chips: 1. Effect of pyrolysis temperature and heating rate on the product yields.* Energy Sources, 2002. **24**(4): p. 347-355.
[5]. Jones, J., et al., *Low temperature ignition of biomass.* Fuel Processing Technology, 2015. **134**: p. 372-377.
[6]. Riaza, J., et al., *Ignition behavior of coal and biomass blends under oxy-firing conditions with steam additions.* Greenhouse Gases: Science and Technology, 2013. **3**(5): p. 397-414.
[7]. Toptas, A., et al., *Combustion behavior of different kinds of torrefied biomass and their blends with lignite.* Bioresource technology, 2015. **177**: p. 328-336.
[8]. Grotkjær, T., et al., *An experimental study of biomass ignition ☆.* Fuel, 2003. **82**(7): p. 825-833.
[9]. Li, J., M.C. Paul, and K.M. Czajka, *Studies of Ignition Behavior of Biomass Particles in a Down-Fire Reactor for Improving Co-firing Performance.* Energy & Fuels, 2016. **30**(7): p. 5870-5877.
[10].Tetteh, J., E. Metcalfe, and S.L. Howells, *Optimisation of radial basis and backpropagation neural networks for modelling auto-ignition temperature by quantitative-structure property relationships.* Chemometrics and intelligent laboratory systems, 1996. **32**(2): p. 177-191.
[11].Wang, C.a., et al., *Pyrolysis and combustion characteristics of coals in oxyfuel combustion.* Applied Energy, 2012. **97**: p. 264-273.
[12].Arenillas, A., et al., *A TG/DTA study on the effect of coal blending on ignition behaviour.* Journal of Thermal Analysis and Calorimetry, 2004. **76**(2): p. 603-614.
[13].Rath, J. and G. Staudinger, *Cracking reactions of tar from pyrolysis of spruce wood.* Fuel, 2001. **80**(10): p. 1379-1389.
[14].Fang, X., L. Jia, and L. Yin, *A weighted average global process model based on two− stage kinetic scheme for biomass combustion.* Biomass and Bioenergy, 2013. **48**: p. 43-50.
[15].Wang, G., et al., *Characterisation and model fitting kinetic analysis of coal/biomass co-combustion.* Thermochimica Acta, 2014. **591**: p. 68-74.
[16].Gil, M.V., et al., *Thermal behaviour and kinetics of coal/biomass blends during co-combustion.* Bioresource Technology, 2010. **101**(14): p. 5601-5608.
[17].Shi, H., *Kinetic study of fire combustible pyrolysis.* Zhejiang University, Hangzhou, 2004: p. 20-21.
[18].White, J.E., W.J. Catallo, and B.L. Legendre, *Biomass pyrolysis kinetics: a comparative critical review with relevant agricultural residue case studies.* Journal of Analytical and Applied Pyrolysis, 2011. **91**(1): p. 1-33.
[19].Ceylan, S. and Y. Topçu, *Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis.* Bioresource technology, 2014. **156**: p. 182-188.
[20].Garcia-Maraver, A., et al., *Determination and comparison of combustion kinetics parameters of agricultural biomass from olive trees.* Renewable Energy, 2015. **83**: p. 897-904.